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Calculations of the intermolecular potential energy function from the x-ray scattering

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The intermolecular potential energy function has been calculated from the X-ray scattering data of liquid argon. The intergo-differential equation from which the Born-Green-Yvon's theory of liquid state starts has been used. This equation relates the radial distribution function and potential energy function. However, in contrast with the usual BGY theory, a method has been developed to calculate the potential energy function directly from the starting equation without using the superposition approximation.

INTRODUCTION

The intermolecular potential energy function $\phi(r)$ is a basic function from which the theoretical study of a molecular assembly usually starts (Hirschfelder 1954). The study of this function is difficult because purely theoretical calculations involve long and tedious quantum mechanical considerations. Apart from other difficulties inherent in such studies all the steps of this calculations have not yet been worked out fully (Born & Green 1946). This is the main reason why we have as yet no fully satisfactory theory of the liquid state. It is well known that to build up a complete theory of the liquid state from statistical mechanical considerations alone, *i.e.* starting from the integro-differential equations developed by Born, Green & Yvon (1946) and Kirkwood (see Hill 1956), it is necessary to know the potential energy functions accurately and explicitly. Although some model theories obviate the explicit use of these functions, for a more definite knowledge, we can not bypass them. The problem can therefore be broken up in two distinct parts (a) Calculations of the potential energy function, and (b) Actual working up of the theory of the liquid state.

About the second part we already have reliable procedures (Hill 1956). We have ourselves extended the integro-differential approach (Guha 1968, Sengupta & Guha 1972) to the theory and shown that the inconsistencies, which lead to errors in calculations of the fourth virial co-efficients for imperfect gases, can be systematically removed by iteration; and thus we have eliminated the major criticism against the theory.

Regarding the first part of the problem, pending detailed theoretical studies, we suggest that for the time being, the molecular potential energy curve

be calculated from straightforward experimental considerations. The expressions thus obtained could be used for constructing the liquid state theory. Most of the existing determinations of the potential energy function from virial co-efficients of the imperfect gases (or from some similar equivalent starting points), and the usual theoretical expressions of such quantities contain potential energy functions under the integral sign. This forces one to assume *a priori* semi-empirical forms in which the parameters have to be adjusted This is an obvious limitation to the method.

The statistical mechanical theory of liquid state, starts from integro-differential equations relating the radial distribution function (and other multiple distribution functions) (Hirschfelder 1954) with the potential energy function Using the superposition and trans-superposition (Fisher 1964) approximations, the theory is tolerably good for calculation of thermodynamical properties and describing the phase transitions With the use of the superposition approximation the result for the third and fourth virial co-efficient shows an error of 20%.

Our suggestion in this paper is based on the observation that the radial distribution functions obtained from the kinetic statistical mechanical theories is really an experimentally determinable function (Gingrich *et al* 1942) The radial distribution function obtained from the Fourier transformation of the experimentally determinable intensity data of the X-ray scattering can provide the necessary basis for calculations of the potential energy function (Thomson *et al* 1968)

In this paper we have shown how to calculate the potential energy function using the Born-Green-Yvon's starting equation (equation 1, see later) using X-ray scattering data. We have developed an iterative method which could be used to improve the result for the potential energy function to any desired degree of approximation The resulting function could then be fed into the starting integrodifferential equations and theory for the assembly could be developed in a straightforward manner and the major thermodynamical quantities for liquids calculated therefrom checked with observational data.

There has been some previous calculations along similar lines *e.g.* by Jhonson and March (1963) However these authors use the usual BGY theory (equation 3, see later or some equivalent) and hence their results are limited by superposition approximation.

1. Method of Calculation

The integro-differential equation relating to the potential energy function and the distribution function in a molecular assembly can be written as (Hirschfelder 1954), using $h = 2$

$$kT \frac{\partial \ln n^{(2)}}{\partial \boldsymbol{r}_1}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{\partial \phi}{\partial \boldsymbol{r}_1}(\boldsymbol{r}_1, \boldsymbol{r}_2) - \int \frac{\partial \phi(\boldsymbol{r}_1, \boldsymbol{r}_3)}{\partial \boldsymbol{r}_1} \frac{n^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)}{n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)} \, d\boldsymbol{r}_3 \qquad (1)$$

where $n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ = Distribution function for a pair of molecules

$\phi(r_{12})$ = Potential energy function for the pair of molecules at a distance r_{12}

$n^{(2)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$ = Distribution function for three molecules

$\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3$ = are the usual distance vectors

k = Boltzman Constant and T = Temperature in °K

The usual theories of liquid state use the superposition approximation, *i e*,

$$n^{(3)}n^{(3)}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3) = n^{(2)}(r_{12})n^{(2)}(r_{13})n^{(2)}(r_{23})$$

where $n^{(2)}$ are functions only of relative coordinates, we integrate eq (1) and use the limiting value $n^{(2)}$ which tends to n^2 at $r_{12}\to\infty$. The radial distribution function $g(r)$ is defined as

$$g(r) = \frac{}{n^2} \quad [n = \text{Average density}], \text{ so that we have,}$$

$$kT \ln g(r) = -\phi(r) + 2\pi n \int_0^{\infty} \int_{r-r_{12}}^{r+r_{12}} \frac{\partial \phi(r_{13})}{\partial r_{13}} [g(r_{23})-1]\, g(r_{13} \times \left[\frac{r_{13}^2-(r_{23}-r)^2}{2r}\right] r_{23}\, dr_{23}\, dr_{13} \tag{2}$$

Putting,

$$\boldsymbol{r} = \boldsymbol{r}_1-\boldsymbol{r}_2, \ \boldsymbol{s} = \boldsymbol{r}_1-\boldsymbol{r}_3, \ \boldsymbol{t} = \boldsymbol{r}_2-\boldsymbol{r}_3,$$

$$kT \ln g(r) = -\phi(r) + \frac{\pi n}{} \int ds g(s) \frac{\partial \phi(s)}{\partial s} \int_{r-s}^{r+s} dx(s^2-t^2)x \times [g(x)-1] \tag{3}$$

where $\boldsymbol{x} = \boldsymbol{t}+\boldsymbol{r}$

Equation (3) is the usual starting point of the Born & Green's (1946) calculations. For our present purpose however, we shall utilize equation (1) itself Since in our case $g(r)$ is assumed to be known experimentally, $\phi(r)$ to first approximation is simply

$$\phi(r) = -kT \ln g(r) \tag{4}$$

As mentioned earlier, $g(r)$ can be calculated from the X-ray diffraction data Further refinement to the calculations can easily be made by iteration. Successive iterative steps needed are shown in the appendix, and it is to be remembered that the analysis in appendix starts from equation (1) itself and is not limited by the superposition approximation (Born & Green 1946)

We have used the above method for calculating the interaction potential energy function for argon. The X-ray scattering data have been given by Thomson *et al* (1968). The radial distribution function has been calculated by taking Fourier transform of the experimental data.

The first approximation to $\phi(r)$ by equation (4) is straightforward. This has been shown graphically as curve (1) in figure 1. Curve $(L-J)$ (2) and curve $(D-J)$ (3) in figure 1 are the curves of the interaction functions computed by Lennard Jones and Dobbs & Jones (1957) respectively.

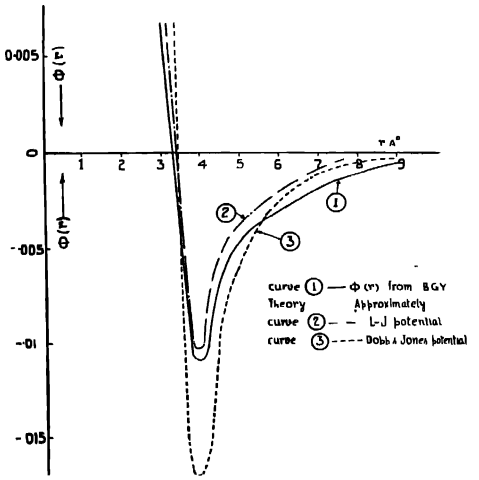

Figure 1. Potential energy function $\phi(r)$ against r in Å for liquid argon at 84.5°K Calculated in first approximation (Equation-4), compared with Dobbs-Jones potential and Lennard-Jones potential.

If we proceed to next refinement we have to compute the integral occuring in the equation A-1 in the appendix. While performing this we took recourse to the numerical integration by trapezoidal rule. Since grid size used is 1Å and since the $rg(r)$ function started from zero and became almost negligible at our last data, the error committed in the integration step is very small. The curve for $\phi(r)$ to this order of accuracy has been drawn in figure 2.

For argon which has been studied in the present paper the Van der waal's interaction is small and we did not find the necessity of refining our calculation beyond the second step. However, for polar molecules the number of steps needed may be considerably larger. In figure 1 the potential energy calculated to first approximation has been compared with Lennard Jones and Dobbs & Jones (1957) function. Figure 2 depicts the same function for the second approximation calculations. We should remember that both the Lennard Jones and Dobb & Jones functions are semi-empirical in nature, the form of the function chosen from initiative considerations with the parameter fitted with gas data.

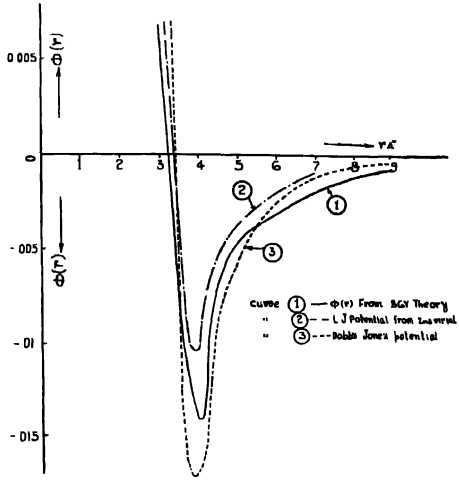

Figure 2. Potential energy function $\phi(r)$ against r in Å for liquid argon at 84.5°K. Calculated in second approximation (Equation-3) and compared with Dobbs-Jones potential and Lennard-Jones potential.

Appendix

The integro-differential equation can be written in the first approximation from.

$$kT\,\frac{\partial \ln n^{(h)}}{\partial \boldsymbol{r}_i}\,(\boldsymbol{r}^h) = -\frac{\partial \phi(\boldsymbol{r}^h)}{\partial \boldsymbol{r}_i} - \int \frac{\partial \phi_{i,h+1}}{\partial \boldsymbol{r}_1}\cdot\frac{n^{(h+1)}}{n^{(h)}}\,d\boldsymbol{r}_{h+1} \qquad \ldots \text{ (A)}$$

as.

$$kT\,\frac{\partial \ln n^{(h)}}{\partial \boldsymbol{r}_{ih}}\,(\boldsymbol{r}^h) = -\frac{\partial \phi(\boldsymbol{r}^h)}{\partial \boldsymbol{r}_{ih}}$$

or,

$$\phi_0(\boldsymbol{r}^h) = -kT \ln \frac{n^{(h)}(\boldsymbol{r}^h)}{n^h} = -\alpha_0{}^{(h)}$$

or,

$$n_0{}^{(h)}(\boldsymbol{r}^h) = n^h \exp(-\alpha_0{}^{(h)}, kT)$$

or,

$$\frac{n_0{}^{(h+1)}(\boldsymbol{r}^{h+1})}{n_0{}^{(h)}(\boldsymbol{r}^h)} = n \exp\left(-\alpha_0{}^{(h+1)} - \alpha_0{}^{(h)}\right)/kT$$

$$= \chi_0{}^{(h+1)} \qquad \ldots \text{ (A-1)}$$

Putting (A-1) in (A) of the text.

$$kT\,\frac{\ln n^{(s^h)}(\mathbf{r}^h)}{n^h} = -\phi(\mathbf{r}^h) - 2\pi\int\int\int \frac{\partial\phi_0(r_{i,\,h+1})}{\partial r_{i,\,h+1}}\,\chi_0^{(h+1)}$$

$$\times\left(\frac{r^2_{ih}+r^2_{i,\,h+1}-r^2_{h,\,h+1}}{2r^2_{ih}}\right) r_{h,\,h+1}\,dr_{i,\,h+1}\,dr_{h,\,h+1}\,dr_{ih}$$

or, $$\phi_1(\mathbf{r}^h) = -kT\ln g_1(\mathbf{r}^h) + 2\pi\int\int\int \frac{\partial\phi_0(r_{i,\,h+1})}{\partial r_{i,\,h+1}}\,\chi_0^{(h^2-1)}$$

$$\times\left(\frac{r^2_{ih}+r^2_{i,\,h+1}-r^2_{h,\,h+1}}{2\gamma_{ih}{}^2}\right) r_{h,\,h+1}\,dr_{i,\,h+1}\,dr_{h,\,h+1}\,dr_{ih}$$

$$= -\alpha_0^{(h)} - \alpha_1{}^{(h)}.$$

where

$$\alpha_1{}^{(h)} = -2\pi\int\int\int \frac{\partial\phi_0(r_{i,\,h+1})}{\partial r_{i,\,n+1}}\,\chi_0^{(h+1)}\left(\frac{r^2_{i\,h+1}+r_h{}^2-r^2_{h,\,h+1}}{2r_{ih}{}^2}\right)$$

$$\times r_{h,\,h+1}\,dr_{ih}\,dr_{h,\,h+1}\,dr_{i,\,h+1}.$$

The quantity $\alpha_1(h)$ is the first correction to the interaction potential. For systems with radial symmetry and under superposition approximation, for $h = 2$, we obtain,

$$\alpha_1{}^{(2)} = \frac{\pi n}{r}\int_0^\infty ds\,g(s)\,\frac{\partial\phi(s)}{\partial s}\int_{r-s}^{r+s} dx(s^2-t^2)x[g(x)-1] \qquad \ldots\ (A\text{-}3)$$

This is the expression (A-3) which have been used in text to calculate the potential energy function for argon. For further refinement we can proceed as follows,

$$\phi_2(\mathbf{r}^h) = -\alpha_0^{(h)} - \alpha_1{}^{(h)} - \alpha_{(2)}{}^{(h)}.$$

$$\phi_3(\mathbf{r}^h) = -\alpha_0^{(h)} - \alpha_1{}^{(h)} - \alpha_{(2)}{}^{(h)} - \alpha_3{}^{(h)}.$$

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$$\phi_n(\mathbf{r}^h) = -\alpha_0^{(h)} - \alpha_1{}^{(h)} \ldots - \alpha_n{}^{(h)}.$$

$\alpha_n{}^{(h)}$ can be found by successive iteration. More explicitly,

$$\alpha_n{}^{(h)} = -2\pi\int\int\int \frac{\partial}{\partial r_{ih}}\,(\alpha_0^{(h)} + \ldots + \alpha_{n-1}{}^{(h)})\chi_{n-1}{}^{(h)} dr_{ih}\times dr_{h,\,h+1}\,dr_{i,\,h+1}.$$

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